

**What is claimed is:**

1. A method of adjusting an electrochemical bath in an electrochemical deposition system, comprising identifying one or more constituents generated during the electrochemical deposition process and adding the one or more constituents to the electrochemical bath.
2. The method of claim 1, wherein identifying one or more constituents generated during the electrochemical deposition process comprises:
  - analyzing at least a portion of a first electrochemical bath to determine a first bath composition;
  - analyzing at least a portion of a second electrochemical bath produced from utilizing the first electrochemical bath in an electrochemical deposition process to determine a second bath composition; and
  - comparing the first and second bath compositions to identify some of the one or more constituents generated in the electrochemical deposition process.
3. The method of claim 2, wherein at least a portion of the first electrochemical bath is directed to a chemical analyzer, wherein the chemical analyzer module analyses the portion of the first electrochemical bath by a high-performance liquid chromatography process.
4. The method of claim 2, wherein at least a portion of the second electrochemical bath is directed to a chemical analyzer, wherein the chemical analyzer module analyses the portion of the second electrochemical bath by a high-performance liquid chromatography process.
5. The method of claim 2, wherein the first electrochemical bath is an electroplating bath.

6. The method of claim 2, wherein the first electrochemical bath is an electroless bath.
7. A method of adjusting an electrochemical bath in an electrochemical deposition process, comprising:
  - a) providing a first electrochemical bath having a first bath composition;
  - b) utilizing the first electrochemical bath in an electrochemical deposition process to form a second electrochemical bath having a second bath composition;
  - c) analyzing the first and second bath compositions to identify one or more constituents generated in the electrochemical deposition process; and
  - d) adjusting the one or more constituents to the first bath composition.
8. The method of claim 7, wherein the first electrochemical bath is an electroplating bath.
9. The method of claim 7, wherein the first electrochemical bath is an electroless bath.
10. The method of claim 7, wherein the electrochemical deposition process deposits a metal film on a substrate.
11. The method of claim 10, wherein the metal film comprises a conductive metal selected from the group of copper, aluminum, doped copper, doped aluminum, and combinations thereof.
12. The method of claim 7, wherein analyzing the first and second electrochemical bath compositions comprises directing at least a portion of the first and second electrochemical bath to a chemical analyzer.
13. The method of claim 12, wherein the chemical analyzer module is used to analyze the portion of the first and second electrochemical baths by a high-

performance liquid chromatography process.

14. A method of adjusting an electrochemical bath in an electrochemical deposition system, comprising:

- a) providing a first electrochemical bath;
- b) analyzing at least a portion of the first electrochemical bath to determine a first bath composition;
- c) utilizing the first electrochemical bath in an electrochemical deposition process to form a second electrochemical bath;
- d) analyzing at least a portion of the second electrochemical bath to determine a second bath composition;
- e) comparing the first and second bath compositions to identify one or more constituents generated in the electrochemical deposition process; and
- f) adding the one or more constituents to the first bath composition.

15. The method of claim 14, wherein the first electrochemical bath is an electroplating bath.

16. The method of claim 14, wherein the first electrochemical bath is an electroless bath.

17. The method of claim 14, wherein analyzing the portion of the first electrochemical bath comprises directing the portion of the first electrochemical bath to a chemical analyzer module and analyzing the portion of the first electrochemical bath by a high-performance liquid chromatography process.

18. The method of claim 14, wherein analyzing the portion of the second electrochemical bath comprises directing the portion of the second electrochemical bath to the chemical analyzer module and analyzing the portion of the second electrochemical bath by a high-performance liquid chromatography process.

19. The method of claim 14, wherein the electrochemical deposition process deposits a metal film on a substrate.

20. The method of claim 19, wherein the metal film comprises a conductive metal selected from the group of copper, aluminum, doped copper, doped aluminum, and combinations thereof.

21. The method of claim 14, wherein comparing the first and second bath compositions to identify one or more constituents generated in the electrochemical deposition process comprises comparing the analyses of the first and second electrochemical baths.

22. A method of adjusting an electrochemical bath for an electrochemical deposition process, comprising:

- a) providing a first electrochemical bath having a first bath composition;
- b) utilizing the first electrochemical bath in an electrochemical deposition process to form a second electrochemical bath having a second bath composition comprising one or more generated constituents;
- c) identifying at least some of the one or more generated constituents by analyzing the first and second bath compositions; and
- d) adding an additive material having a composition that is substantially the same as at least some of the one or more generated constituents to a third electrochemical bath to form a fourth electrochemical bath.

23. The method of claim 22, wherein the third electrochemical bath has the composition of the first electrochemical bath.

24. The method of claim 22, wherein identifying at least some of the one or more constituents generated during the electrochemical deposition process comprises:

analyzing at least a portion of the first electrochemical bath to determine the first bath composition;

analyzing at least a portion of the second electrochemical bath produced from utilizing the first electrochemical bath in the electrochemical deposition process to determine the second bath composition; and

comparing the first and second bath compositions to identify at least some of the one or more constituents generated in the electrochemical deposition process.

25. The method of claim 24, wherein at least a portion of the first electrochemical bath is directed to a chemical analyzer, wherein the chemical analyzer module analyses the portion of the first electrochemical bath by a high-performance liquid chromatography process.

26. The method of claim 24, wherein at least a portion of the second electrochemical bath is directed to a chemical analyzer, wherein the chemical analyzer module analyses the portion of the second electrochemical bath by a high-performance liquid chromatography process.

27. The method of claim 22, wherein the first electrochemical bath is an electroplating bath.

28. The method of claim 22, wherein the first electrochemical bath is an electroless bath.

29. A method of electrochemical deposition of a metal on a substrate, comprising:

- a) providing an electrochemical bath comprising:
  - 1) an electrolyte; and
  - 2) an additive material having a composition that is substantially the same as at least some of one or more constituents identified as being generated from an electrochemical deposition process;
- b) depositing the substrate in the electrochemical bath; and
- c) electrodepositing the metal onto the substrate.

30. The method of claim 29, wherein the metal comprises a conductive metal selected from the group of copper, aluminum, doped copper, doped aluminum, and combinations thereof.

31. The method of claim 29, wherein the electrochemical bath is an electroplating bath.

32. The method of claim 29, wherein the electrochemical bath is an electroless bath.

33. The method of claim 29, wherein the electrolyte solution comprises:

a) metal ions, wherein the metal ions are copper ions provided by a copper salt selected from the group consisting of copper sulfate, copper fluoborate, copper gluconate, copper sulfamate, copper sulfonate, copper pyrophosphate, copper chloride, copper cyanide, and mixtures thereof; and

b) supporting electrolytes selected from sulfuric acid, sulfamic acid, fluoboric acid, sulfonic acid, hydrochloric acid, nitric acid, perchloric acid, gluconic acid, and combinations thereof.

34. The method of claim 33, wherein the electrochemical bath further comprises one or more additives selected from the group consisting of surfactants, levellers, brighteners, grain refines, and combinations thereof.

35. A method of electrochemical deposition of a metal on a substrate, comprising:

- a) providing a first electrochemical bath having a first composition;
- b) utilizing the first electrochemical bath in an electrochemical deposition process to form a second electrochemical bath having a second composition comprising one or more generated constituents;
- c) identifying at least some of the one or more generated constituents by analyzing the first and second compositions;

- d) adding an additive material having a composition that is substantially the same as at least some of the one or more generated constituents to a third electrochemical bath to form a fourth electrochemical bath;
- e) depositing the substrate in the fourth electrochemical bath; and
- f) electrodepositing the metal onto the substrate.

36. The method of claim 37, wherein identifying at least some of the one or more constituents generated during the electrochemical deposition process comprises:

analyzing at least a portion of the first electrochemical bath to determine the first bath composition;

analyzing at least a portion of the second electrochemical bath produced from utilizing the first electrochemical bath in the electrochemical deposition process to determine the second bath composition; and

comparing the first and second bath compositions to identify at least some of the one or more constituents generated in the electrochemical deposition process.

37. The method of claim 36, wherein at least a portion of the first electrochemical bath is directed to a chemical analyzer, wherein the chemical analyzer module analyses the portion of the first electrochemical bath by a high-performance liquid chromatography process.

38. The method of claim 36, wherein at least a portion of the second electrochemical bath is directed to a chemical analyzer, wherein the chemical analyzer module analyses the portion of the second electrochemical bath by a high-performance liquid chromatography process.

39. The method of claim 35, wherein the metal comprises a conductive metal selected from the group of copper, aluminum, doped copper, doped aluminum, and combinations thereof.

40. The method of claim 35, wherein the first electrochemical bath is an

electroplating bath.

41. The method of claim 35, wherein the first electrochemical bath is an electroless bath.

42. The method of claim 35, wherein the additive material having a composition that is substantially the same as at least some of the one or more generated constituents is provided to the third electrochemical bath prior to electrodepositing the metal onto the substrate.

43. The method of claim 35, wherein the additive material having a composition that is substantially the same as at least some of the one or more generated constituents is provided to the third electrochemical bath during electrodepositing the metal onto the substrate.

44. The method of claim 35, wherein the additive material having a composition that is substantially the same as at least some of the one or more generated constituents is added periodically during electrodepositing the metal onto the substrate.

45. The method of claim 35, wherein the additive material having a composition that is substantially the same as at least some of the one or more generated constituents is added continuously during electrodepositing the metal onto the substrate.

46. An electrochemical deposition process, comprising:

adding one or more selected chemical constituents to a primary electrochemical bath; and

electrodepositing metal on a substrate contained in the primary electrochemical bath, wherein the one or more chemical constituents added to the primary electrochemical bath are identified as being generated during an



electrochemical deposition process by comparing the compositions of at least two other electrochemical baths with one another.

47. The electrochemical deposition process of claim 46, wherein the primary electrochemical bath in which the substrate is contained during the electrodeposition process includes one or more of the selected chemical constituents.

48. The electrochemical deposition process of claim 46, wherein the one or more chemical constituents are generated in an electrochemical deposition process.

49. The electrochemical deposition process of claim 46, wherein the primary electrochemical bath in which the substrate is contained during the electrodeposition process includes reactant by-products of the selected chemical constituents.

50. The electrochemical deposition process of claim 46, wherein comparing the compositions of the at least two other electrochemical baths includes determining at least one composition profile corresponding to each of the other electrochemical baths and determining chemical constituents that are present in one electrochemical bath and not present in another electrochemical bath.

51. The electrochemical deposition process of claim 46, further comprising analyzing at least one of the electrochemical baths using HPLC before comparing that electrochemical bath to a reference composition.

52. The electrochemical deposition process of claim 46, wherein the metal being electrodeposited on the substrate comprises a conducting metal selected from the group consisting of copper, nickel, and combinations thereof.

53. A method of adjusting an electrochemical bath in an electrochemical deposition system, comprising:

- a) providing a first copper electroplating bath;
- b) analyzing a first portion of the first copper electroplating bath to determine a first bath composition by directing the first portion of the first copper electroplating bath to a chemical analyzer module and separating and identifying constituents of the first copper electroplating bath by a high-performance liquid chromatography process;
- c) utilizing a second portion of the first copper electroplating bath in a copper electroplating process to form a second copper electroplating bath;
- d) analyzing a portion of the second copper electroplating bath to determine a second copper electroplating bath composition by directing the portion of the second copper electroplating bath to a chemical analyzer module and separating and identifying constituents of the second copper electroplating bath by a high-performance liquid chromatography process;
- e) comparing the constituents of the first and second copper electroplating bath compositions to identify one or more constituents generated in the copper electroplating process; and
- f) adding the one or more constituents generated in the copper electroplating process to the first copper electroplating bath.

54. A method of adjusting an electrochemical bath for an electrochemical deposition process, comprising:

- a) providing a first copper electroless bath having a first bath composition;
- b) utilizing a portion of the first copper electroless bath in an electroless deposition process to form a second copper electroless bath having a second copper electroless bath composition comprising one or more generated constituents;
- c) identifying at least some of the one or more generated constituents by determining the first and second copper electroless bath compositions, wherein identifying at least some of the one or more constituents generated during the electrochemical deposition process comprises:
  - (i) analyzing a portion of the first copper electroless bath to

determine the first bath composition;

(ii) analyzing a portion of the second copper electroless bath to determine the second bath composition; and

(iii) comparing the first and second copper electroless bath compositions to identify at least some of the one or more constituents generated in the electroless deposition process; and

d) adding an additive material having a composition that is substantially the same as at least some of the one or more generated constituents to a third copper electroless bath to form a fourth copper electroless bath.

55. The method of claim 54, wherein the third copper electroless bath has the composition of the first copper electroless bath.

56. The method of claim 54, wherein analyzing a portion of the first copper electroless bath comprises directing the portion of the first copper electroless bath is directed to a chemical analyzer and separating and identifying constituents of the first copper electroless bath by a high-performance liquid chromatography process.

57. The method of claim 54, wherein analyzing a portion of the second copper electroless bath comprises directing at least a portion of the first copper electroless bath is directed to a chemical analyzer and separating and identifying constituents of the second copper electroless bath by a high-performance liquid chromatography process.